Predicting soil acidification trends at Plynlimon using the SAFE model

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Abstract

The SAFE model has been applied to an acid grassland site, located on base-poor stagnopodzol soils derived from Lower Palaeozoic greywackes. The model predicts that acidification of the soil has occurred in response to increased acid deposition following the industrial revolution. Limited recovery is predicted following the decline in sulphur deposition during the mid to late 1970s. Reducing excess sulphur and NO_x deposition in 1998 to 40% and 70% of 1980 levels results in further recovery but soil chemical conditions (base saturation, soil water pH and ANC) do not return to values predicted in pre-industrial times. The SAFE model predicts that critical loads (expressed in terms of the (Ca+Mg+K):Al_{crit} ratio) for six vegetation species found in acid grassland communities are not exceeded despite the increase in deposited acidity following the industrial revolution. The relative growth response of selected vegetation species characteristic of acid grassland swards has been predicted using a damage function linking growth to soil solution base cation to aluminium ratio. The results show that very small growth reductions can be expected for 'acid tolerant' plants growing in acid upland soils. For more sensitive species such as *Holcus lanatus*, SAFE predicts that growth would have been reduced by about 20% between 1951 and 1983, when acid inputs were greatest. Recovery to c. 90% of normal growth (under laboratory conditions) is predicted as acidic inputs decline.

Introduction

The concept of critical loads has been developed as a tool to provide environmentally-based abatement strategies for the emissions of gaseous pollutants arising from the combustion of fossil fuels and the intensification of agriculture (DOE 1994). The concept relies on setting a threshold value for pollutant deposition to a chosen receptor which will just not cause chemical changes leading to long-term ecological damage (Bull 1991). Whilst the concept is a simple one, the practical task of setting critical loads for ecological targets is much more complex. As a consequence, various approaches have been adopted, including empirical classifications (e.g. Nilsson and Grennfelt 1988), simple mass balance equations (e.g. Sverdrup and De Vries 1994), and steady state and dynamic process models (e.g. Sverdrup and Warfvinge 1993a; DeVries *et al.* 1994; Sverdrup *et al.* 1995). The critical loads approach is a cornerstone for the ongoing UNECE negotiations on pollutant gas emissions across Europe (Grennfelt *et al.* 1994); thus, there is a requirement for information describing the critical loads of various air pollutants across the UK.

Plant roots are generally used as the biological target for the calculation of the critical load for the soil-plant system and the chemical threshold is usually set in terms of the (Ca+Mg+K):Al_{crit} ratio in soil solution at which root damage occurs. Recently, data on the relationship between growth and (Ca + Mg + K):Al_{crit} ratio has been assembled for a range of tree and ground flora species (Sverdrup and Warfvinge 1993b); this allows thresholds to be set and critical loads to be calculated for a range of soil-plant systems.

To date, critical loads and critical loads exceedance have been considered in terms of equilibrium (steady-state) conditions. In reality, the systems are dynamic and will show different rates of response to changes in deposition. As the levels of different pollutants are changing, it is important that these differences are taken into account. The output from dynamic models can be linked to the critical loads' concept via the specified (Ca + Mg + K):Al_{crit} ratio for the target species. Changes in soil solution chemistry can also be linked to plant response functions (again using the (Ca + Mg + K):Al_{crit}) to predict changes in vegetation growth over time (Sverdrup and Warfvinge 1993b).

This paper reports the application of the SAFE dynamic acidification model to a representative soil profile within an upland acid grassland catchment at Plynlimon for which there is a wealth of background data. The response of various indices of soil acidification (e.g. soil water ANC, base saturation) to changing acid deposition scenarios are predicted. Predicted changes in the (Ca + Mg + K):Al ratio are linked to plant growth response using a simple damage function proposed by Sverdrup and Warfvinge (1993b).

Background to the SAFE Model

The SAFE model is a dynamic geochemical model which calculates weathering release of base cations (Ca + Mg + K) and changes in soil solution chemistry and base saturation (strictly Ca + Mg + K saturation) in response to changes over time in atmospheric deposition, net nutrient uptake, nutrient cycling and hydrology (Warfvinge *et al* 1993; Jonnsson 1994). For input, the model uses measurable properties such as soil texture, mineralogy, soil moisture conditions together with time series of atmospheric deposition, net nutrient uptake, nutrient cycling and hydrology. Within the model, the soil profile is divided into several layers which correspond to the natural soil horizons. Each soil layer is treated as a perfectly mixed-tank reactor.

Mineral weathering within SAFE relies on the hypothesis that the surface reactions of minerals follow universal rate laws even though the chemical environment of the mineral may vary. The weathering rate for the soil profile is the sum of the dissolution rates for the individual minerals. Dissolution rates increase in response to increasing concentrations of hydrogen ions, organic acids and higher partial pressures of CO_2. Dissolution rates are inhibited by the accumulation of weathering products such as inorganic aluminium and base cations. Temperature dependence of weathering reactions is expressed using an Arrehenius equation. Soil water saturation is used to estimate the fraction of the exposed mineral surface area in contact with water and thus able to participate in weathering reactions. The weathering of secondary minerals is represented by the dissolution of vermiculite.

Inorganic aluminium concentrations are modelled by assuming that soil water concentrations of Al^{3+} are controlled by equilibrium with the mineral gibbsite. This pragmatic approach is acknowledged as controversial and an alternative is currently under development (Jonsson 1994). Soil water concentrations of dissolved organic carbon are specified as input. Whilst DOC participates in the formation of weak acids, it does not enter complexation reactions with aluminium.

The SAFE model calculates cation exchange reactions as reversible chemical reactions which are rate limited by the transport of base cations through the soil solution. A Gapon exchange equation is used to model the base cation concentration at the exchange surface. The nutrient base cations (Ca+Mg+K) are modelled as a lumped divalent component. This is not a true representation of the K exchange reaction but introduces only a small error given that the Gapon equation regards the exchange surface as monovalent. This simplification is a necessary compromise between the exact representation of reaction mechanisms, model complexity and the useful predictive capability of the model. An important feature of the version of the model (SAFE v. 0.0B9) used here is that it calibrates to known values of base saturation. Any number of values may be used as calibration points. Having achieved a successful calibration, the model then develops a 'hindcast' of soil solution chemistry and base saturation from the calibration points to the starting date of the input time-series. It also predicts forward to the end of the input time-series.

In the SAFE model, all nitrogen is considered to be deposited as nitrate, which is equivalent to assuming complete nitrification in the surface soil layer. Denitrification is not included in the model. SAFE was originally designed for application to recently developed soils in glaciated regions. For this reason, it does not include sulphate adsorption reactions.

The representation of a simplified nutrient cycle is an important feature of SAFE. Nutrient cycling is considered with respect to inputs and outputs from the soil where:

$$TI = Wd + Dd + Ce + Lf + Nm \quad (1)$$

and

$$TO = Nu + Ce + Lf \quad (2)$$

where:

TI = Total input
Wd = Wet deposition
Dd = Dry deposition
Ce = Canopy exchange
Lf = Litter fall
Nm = Net mineralisation
TO = Total output
Nu = net uptake (uptake into growth of stems, branches and coarse roots)
All terms are in meq m^{-2} $year^{-1}$.

Canopy exchange is calculated as the difference between throughfall and (wet + dry) deposition. Litter fall is the leachable nutrient content of falling needles or leaves. Net mineralisation is the net supply or accumulation of nutrients from the soil organic phase and essentially represents the change in the soil organic matter nutrient pool.

Application of SAFE to an acid grassland stagnopodzol soil at Plynlimon

SOIL PROFILE DATA

The model has been set up using soil parameter data taken from a stagnopodzol soil profile under a semi-natural *Nardus-Festuca* dominated acid grassland community. The profile, which is described in detail in Reynolds *et al.* (1988), is located in the C2 subcatchment of the Upper Wye at an altitude of 435m and is divided into four main horizons. These comprise an organic-rich surface Oh horizon underlain by a leached greyish, heavily textured Eag horizon. Below this is a fine textured podzolic Bs horizon merging into a stoney C horizon. The thickness of each horizon and associated soil data are given in Table 1.

Table 1. Input data for individual soil horizons at Plynlimon.

Parameter	Unit	Oh	Eag	Bs	C
Horizon thickness	m	0.07	0.06	0.16	0.2
Bulk density	kg m^{-3}	769	921	862	862
pCO_2	times ambient	7.5	10	17.5	20
Inflow	% of precipitation	100	85	85	85
Percolation	% of precipitation	85	85	85	85
Ca + Mg + K uptake	% of total max	85	10	5	0
N uptake	% of total max	85	10	5	0
DOC	mg l^{-1}	9.5	6.0	3.7	2.3
pK Gibbsite		6.5	7.5	8.5	9.5
Exposed surface area	m^2 m^{-3}	1e3	3.27e6	2.81e6	3.37e5
CEC	keq kg^{-1}	60.9e–6	66.9e–6	41.3e–6	22.1e–6
Base saturation	%	14.6	8.2	5.6	6.8
Mineral	% of total				
Plagioclase feldpsar		0.0	1.0	1.0	1.0
Muscovite		0.0	58.3	56.6	33.9
Chlorite		0.0	0.1	11.1	12.3
Vermiculite		0.0	0.8	0.2	0.1

Soil bulk density data were obtained from the means of measurements from three profiles dug in the C2 catchment. Samples were collected using standard equipment and techniques recommended by the Soil Survey of England and Wales (Avery and Bascomb, 1974), and values for the fine earth fraction (< 2mm) are given in Table 1. The cation exchange capacity (CEC) was determined on soil samples collected from three profiles within the subcatchment in 1992. Exchangeable base cations were determined by extraction of field moist soil with unbuffered barium chloride solution. Exchangeable acidity was determined by alkali titration to pH 8.3 following extraction with unbuffered potassium chloride. The effective CEC was estimated as the sum of the base cations and the exchangeable acidity.

Values for soil pCO_2 and the gibbsite equilibrium constant were taken from the range of defaults given by Sverdrup *et al.* (1990). Soil water dissolved organic carbon (DOC) concentrations were means of measured values from the site (Reynolds *et al.* 1988). The inflow and percolation of water between horizons were estimates based on the hydrological properties and behaviour of similar soils at Plynlimon and elsewhere in the Welsh uplands (Knapp 1970; Chappell 1990). An evapotranspiration loss of 15% was assumed from the surface soil layer (Kirby *et al.* 1991). Nutrient uptake was distributed amongst the soil horizons in proportion to the distribution of plant roots observed in a soil pit dug at the site (Reynolds *et al.* 1988).The model was set up to run at an annual time-step from 1800 to 2050 and was calibrated to base saturation values measured in 1992.

Soil mineralogy in Table 1 was taken from Chapman (1986), amended to include a small percentage of plagioclase feldspar on the basis of mineralogical data from elsewhere in Wales for soils developed from similar parent materials (Evans 1973). The mineral composition for each horizon is expressed on a percentage by weight basis for the fine earth (< 2mm) fraction. The model's requirements are for a surface area-weighted mineralogy. This could not be achieved as mineral data were not available for all the size fractions of the soil.

The main clay mineral present in the soil at Plynlimon is illite. This mineral is not contained within SAFE so the illite fraction has been assigned to muscovite. Although the two minerals are structurally and chemically similar, several important differences occur. Illites generally contain less potassium but more silicon than muscovite, whilst magnesium may be isomorphously substituted for aluminium in the muscovite lattice. The model assumes congruent dissolution of primary minerals which may not be appropriate for illite leading to incorrect rates of base cation release.

The exposed mineral surface area (Aw) was calculated from particle size data provided by Chapman (1986) using the relationship between soil particle size and surface area proposed by Sverdrup *et al.* (1990), whereby:

$$Aw = (0.3\ Xsand + 2.2\ Xsilt + 8.0\ Xclay)\ \rho bulk \quad (3)$$

where:

$$Xcoarse + Xsand + Xsilt + Xclay = 1 \quad (4)$$

and ρ bulk = bulk density

The size fractions are classified as:

Coarse > 2000 μm
Sand 63–2000 μm
Silt 2–63 μm
Clay < 2 μm

Soil moisture data were obtained from five years of monthly data from a network of seven neutron probe access tubes located in podzol soils throughout the Upper Wye catchment. This gave an average moisture content, aggregated for the whole profile, of 0.43 m^3 m^{-3}. Soil temperature was set to the 10 year (1980–1990) average value measured at 30 cm within the stagnopodzol profile at C2, adjacent to the sites sampled for soil bulk density and mineralogy.

Time Series Variables

Four input variables must be specified through time; atmospheric deposition, rainfall, net nutrient uptake and nutrient cycling parameters.

ATMOSPHERIC DEPOSITION

Atmospheric deposition to the site for 1987–1988 has been modelled to incorporate orographic enhancement of wet deposition, occult deposition, dry deposition of ammonia, NO_2 and SO_2 (Reynolds *et al.* 1997 and Table 2).Using these data as a reference point, the time-series of deposition to the site was constructed as follows. Firstly, it was assumed that the seasalt inputs of sodium, chloride, potassium, magnesium, calcium and sulphate remained constant over time at the modelled 1987/1988 amounts. The seasalt contribution was estimated assuming that all sodium was derived from seasalts. This revealed a small non-seasalt contribution to chloride deposition in 1987/1988 which was removed from the deposition time-series data. Secondly, the deposition modelled in 1987/1988 was held constant until the model calibration year of 1992. This may mean that sulphate deposition is over estimated for 1992, although analysis of trends in deposition chemistry at Plynlimon shows virtually no change in rainfall sulphate concentrations between 1987 and 1992 (Robson and Neal 1996) and rainfall amounts were almost identical during the two periods (1987/1988 and 1992).

Table 2. Atmospheric input data for the Plynlimon acid grassland site for 1987–1988 (after Reynolds *et al.* 1997).

Parameter	Deposition (meq m^{-2} $year^{-1}$)
SO_4	142
Cl	331
NO_3	48
NH_4	120
Ca	30
Mg	65
K	6
Na	282
Al	0

The historic time-series for excess sulphate (SO_4*) deposition was constructed by scaling the modelled 1987/1988 inputs at Plynlimon to a time-series developed for the application of the MAGIC model to Welsh sites (Jenkins and Wright 1992) (Fig. 1a). The time-series for excess calcium deposition was constructed in a similar manner using modelled 1987/1988 excess calcium inputs at Plynlimon scaled to follow the same historical pattern as sulphate (Fig. 1a). This assumes that emissions of calcium from industrial processes and as a result of agricultural intensification (liming) follow the historical progress of industrialisation broadly reflected in the excess sulphate deposition pattern.

The time-series for nitrate and ammonium were rather more difficult to construct as there are few historical data from remote parts of the UK. The time-series chosen were modified versions of historical trends developed for the Aber site in North Wales (Emmett, pers comm 1995), scaled to 1987/1988 modelled deposition at Plynlimon (Fig. 1b). There are large uncertainties surrounding these trends and the size of the modelled NHy input for 1987/1988. The latter is due to the difficulties in obtaining reliable measurements of ammonia gas concentrations and to the problems of modelling the dry deposition of ammonia which forms a large component of the NHy input.

Predictions of future trends in the deposition of acidic pollutants and excess calcium were based on two scenarios. The first of these was 'business as usual' in which the deposition of nitrogen, excess sulphur and excess calcium were held constant at 1987/1988 levels. The second introduced a reduction in excess sulphate deposition with respect to 1980 levels of 20% in 1993, 40% in 1998 and 60% in 2003. These deposition reductions follow the Large Scale Combustion Plant Directive (LCPD) and assume that all emission reductions result in a quantitatively similar deposition reduction at the site. This, clearly an over-simplification, serves to illustrate the model response. The deposition of excess calcium was reduced following the same pattern as excess sulphate.

Reductions in nitrate deposition were simulated alongside those for sulphur incorporating a reduction in deposition with respect to 1980 levels of 15% by 1993 and 30% by 1998. This parallels the LCPD schedule for NOx emissions. In reality, about 50% of NOx emissions originate from automobiles (DOE 1994), so that a 15 or 30% reduction in LCP emissions will not translate to the same percentage reduction in deposition at the modelled site. Nitrate deposition was 'ramped down' from 1992, as a linear reduction between 1980 and 1993 resulted in a lower deposition at the site than that observed for the period 1987 to 1992. Ammonium deposition was held constant at 1987/1988 amounts.

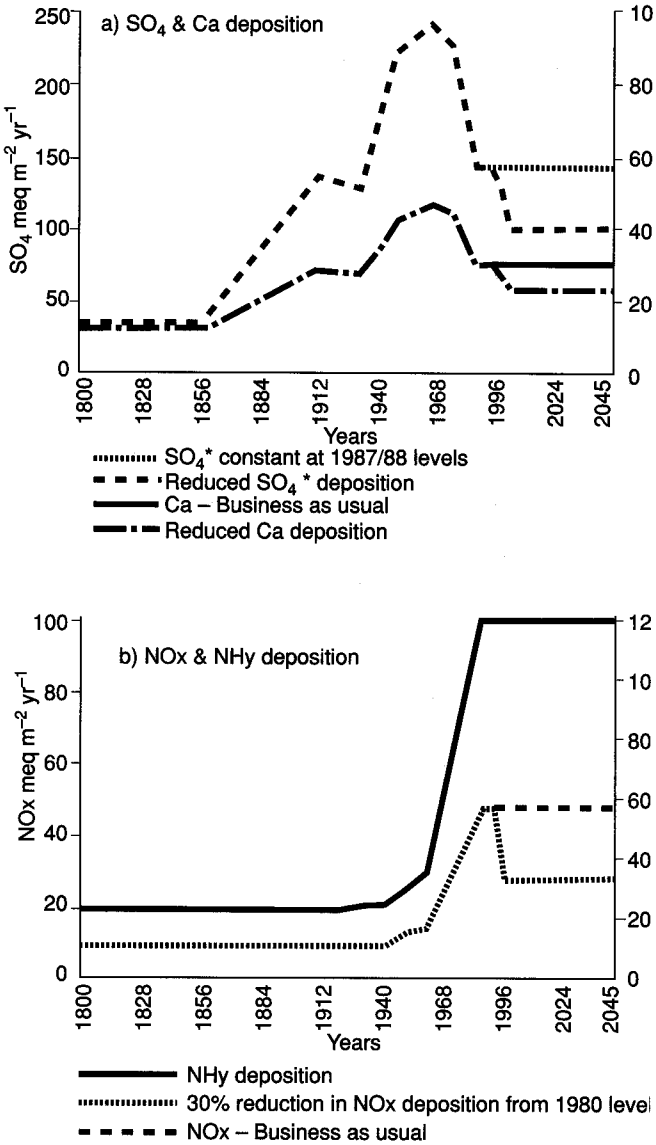

Fig. 1. *Time series of a) sulphate and calcium deposition and b) (NO_3 + NO_2) and (NH_4 + NH_3) deposition.*

RAINFALL

The time-series rainfall input was held constant at the 24 year annual average for the site of 2485 mm.

NET NUTRIENT UPTAKE AND NUTRIENT CYCLING PARAMETERS

For grassland systems in steady-state, the net uptake of nutrients is effectively zero. However, the system is subject to light grazing by sheep (< 2 ewes ha^{-1}), so the maximum net uptake of base cations and nitrogen were each set to a low value of 10 meq m^{-2} $year^{-1}$. SAFE regards the uptake of base cations as a lumped parameter and does not differentiate between the individual cations.

Canopy exchange of calcium and potassium was estimated from ion fluxes in bulk precipitation and from throughfall collected beneath the grass canopy at the site (Reynolds *et al.* 1989). The values for canopy exchange were held constant for the entire time-series. It was assumed that there was no canopy exchange of magnesium. For nitrogen, the grass throughfall data indicates uptake by the canopy. In the model, canopy exchange was assumed to result in a 50% reduction of the incoming nitrogen from deposition.

Litter fall nutrient fluxes were calculated using data from an upland grassland system at Llydaw in North Wales (Heal and Perkins, 1978) and from the moorland adjacent to the forest site at Aber. Net annual above-ground herbage production at Aber was estimated from samples collected in 1994 to be 360 g m^{-2} $year^{-1}$ dry weight. This figure lies at the upper end of estimates from Moorhouse of 116–363 g m^{-2} $year^{-1}$ dry weight for deep peats overlying limestone (Harrison *et al.* 1994).

The nutrient contents of the fresh, above-ground material and litter from Llydaw are shown in Table 3 and are greater than values published by Allen (1989) for samples collected from a wide range of upland sites in Britain. This reflects the relatively high base cation status and fertility of the soils at Llydaw which are derived from base-rich pumice tuff bedrock. In view of this, and the lack of reliable data for magnesium at Llydaw, the litter nutrient content at Plynlimon (Table 4) has been approximated using the data published in Allen (1989) multiplied by the litter/fresh ratio from Llydaw. It is assumed that the ratio for calcium is also applicable to magnesium. The litter fall nutrient fluxes have been held constant over time in the model.

It was assumed that the net mineralisation of base cations by soil organic matter was zero. The net mineralisation term for nitrogen was estimated by mass balance from equations 1 and 2 as a function of nitrogen deposition, nitrogen leaching and net nitrogen uptake (equation 3).

$$Nm = Nu + Le - (Wd + Dd) \quad (3)$$

Under pre-industrial conditions, Nm was calculated as –3 meq m^{-2} yr^{-1} . This assumed that the nitrogen leaching concentration was 8.5 µmol N l^{-1} (50% of current day and comparable to values observed at 'pristine' sites), runoff was 85% of rainfall, total nitrogen deposition was 31 meq m^{-2} yr^{-1} and net uptake was 10 meq m^{-2} yr^{-1}.

In the period 1980–89, the mean soil water nitrate concentration for the entire soil profile at Plynlimon was 17 µmol N l^{-1} (Reynolds *et al.* 1992). Assuming that runoff was 85% of the 24 year annual average rainfall, this gave a value of 36 meq m^{-2} yr^{-1} for Le. Total nitrogen deposition in 1987 was 168 meq m^{-2} yr^{-1} and net uptake was 10 meq m^{-2} yr^{-1}, giving a value of –122 meq m^{-2} yr^{-1} for Nm. Between pre-industrial times and 1987, the annual value for Nm was calculated by scaling the annual value of Le

in proportion to the annual total nitrogen deposition and Nu was held constant at 10 meq m^{-2} yr^{-1}.

Results

The model output comprises time series of annual values of soil base saturation, soil water pH, acid neutralisation capacity (ANC), base cation concentration (Ca + Mg + K) and (Ca + Mg + K):Al_{crit} for each soil horizon. Examples of model output from the soil Bs horizon are shown in Fig. 2 and 3.

Values of all three indices of soil acidification (base saturation, soil water pH and ANC; Fig. 2a, 2b and 3a) drop markedly as the amount of acidic deposition increases from the mid 19th century onwards. With a decline in deposition in the late 1970s to early 1980s, some recovery occurs. This is sustained as excess sulphur and NOx depositions are reduced progressively to 40% and 70% of 1980 levels respectively. However, sub-soil base saturation in 2050 is still less than 50% of pre-industrial values and ANC remains negative and about 40 $\mu eq l^{-1}$ lower than the values initially modelled in 1800.

Weathering rates predicted by SAFE vary by about 10% in response to changes in deposition and nutrient cycling (Fig. 4a). Predicted soil water base cation concentrations also vary by about ± 10% of the 250 year mean of 94 $\mu eq l^{-1}$ (Fig. 4b). Base cation to aluminium ratios decline steeply once acid deposition begins to increase, reaching a minimum of about 3 in the 1970s before recovering to between 6 and 12 by the year 2050 (Fig. 3b). Comparison between the curves in Fig. 3b and 4b suggests that an increase in soil aluminium concentrations is the main factor driving the changes in (Ca+Mg+K):Al ratio.

In general, the patterns observed in the other horizons are similar to those seen in the Bs horizon with limited recovery in base saturation, soil water pH, ANC and (Ca+Mg+K):Al ratio in response to the reduction in acidic inputs.

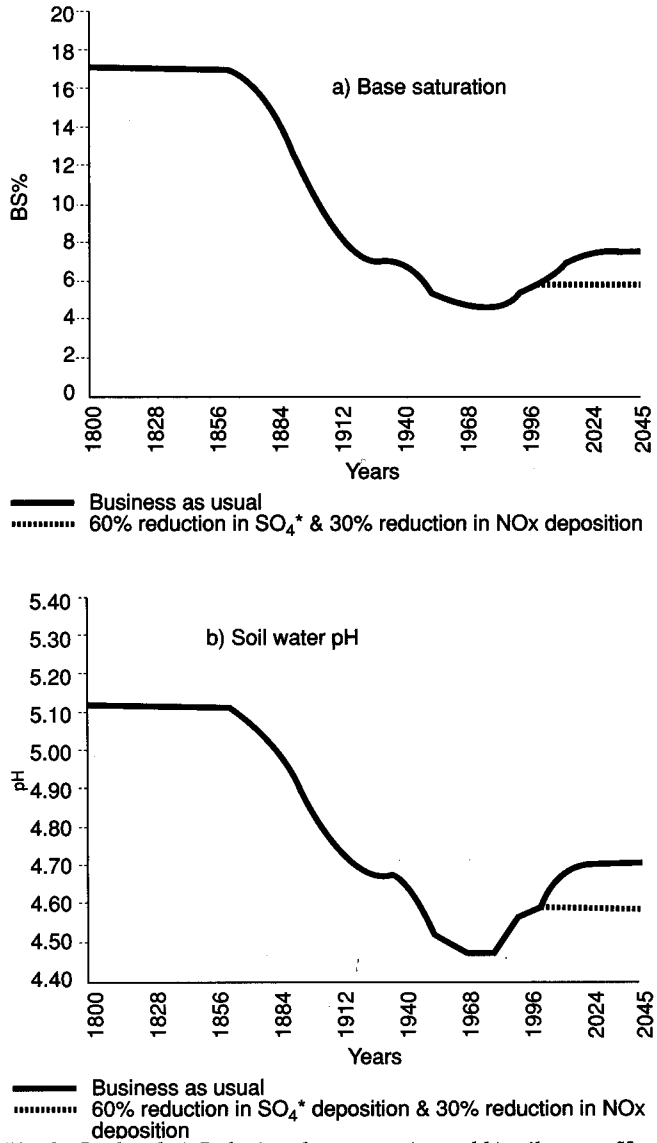

Fig. 2. *Predicted a) Bs horizon base saturation and b) soil water pH for an acid grassland stagnopodzol at Plynlimon.*

Table 3. Nutrient content (mg g^{-1} dry weight) of fresh above ground material and litter from an acid grassland system at Llydaw, North Wales (Heal and Perkins 1978).

	K	Ca	N
Fresh	17.4	4.3	22.9
Litter	4.7	2.0	12.5
Litter/fresh ratio	0.27	0.47	0.54

Table 4. Published base cation contents of aerial growth of Nardus-Festuca grassland and derived values for grass litter at Plynlimon (mg g^{-1} dry weight).

	K	Ca	Mg	N
Nardus-Festuca (Allen *et al.* 1989)	13.5	2.05	0.8	14.5
Plynlimon litter	3.6	0.96	0.37	7.87

CRITICAL CHEMICAL VALUES FOR UPLAND VEGETATION

Critical (Ca+Mg+K):Al ratios are available for several vegetation species that would be found within an upland acid grassland community (Table 5). With the exception of *Holcus lanatus* which is characteristic of less acidic, more fertile upland areas, these species are relatively insensitive to acidification effects expressed as a response to soil water (Ca+Mg+K):Al ratios. The value of (Ca + Mg + K):Al_{crit} is for a reduction in root growth to 80% of 'normal' under laboratory conditions (Sverdrup and Warfvinge 1993b).

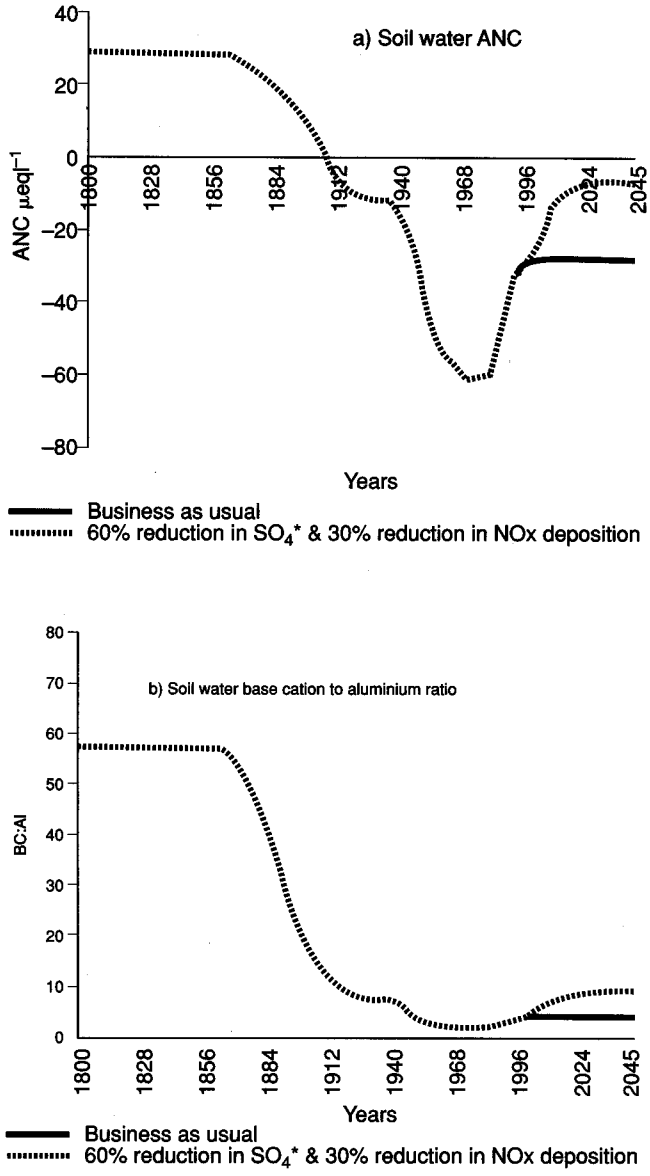

Fig. 3. *Predicted a) Bs horizon soil water ANC and b) soil water base cation to aluminium ratio for an acid grassland stagnopodzol at Plynlimon.*

The roots of the majority of grassland vegetation occur in the Oh horizon, although rooting is not uncommon at depth in the Bs horizon. The time-series of (Ca + Mg + K):Al ratio for the Oh is plotted in Fig. 5a and shows that all species in Table 5 except *Holcus lanatus* would be protected under the acid deposition scenarios modelled at Plynlimon. SAFE predicts that the value of (Ca + Mg + K):Al is less than 8 in the Oh horizon between 1948 and 1985, reaching a minimum of 5.70 in 1968. In contrast, for the Bs horizon (Fig. 3b), the ratio drops below 8 in 1938, declining to a minimum of 2.76 in 1974. Although recovery occurs, the ratio never exceeds 8 under the 'business as usual' scenario, although it exceeds 8 by 2012 in response to deposition reductions. The model therefore predicts some limitation in the growth of *Holcus lanatus* in acid upland grassland swards in response to acidic deposition.

The reduction in vegetation growth in response to changing (Ca + Mg + K):Al ratios in the soil solution can be modelled using a damage function developed by Sverdrup and Warfvinge (1993b). The damage function uses an ion exchange model to simulate the interaction between base cations and aluminium at the root surface. The ion exchange model is linked to the root damage function via an experimentally determined coefficient (K). Several ion exchange models are available including Gaines-Thomas, Gapon, Vanselow and Unspecific and

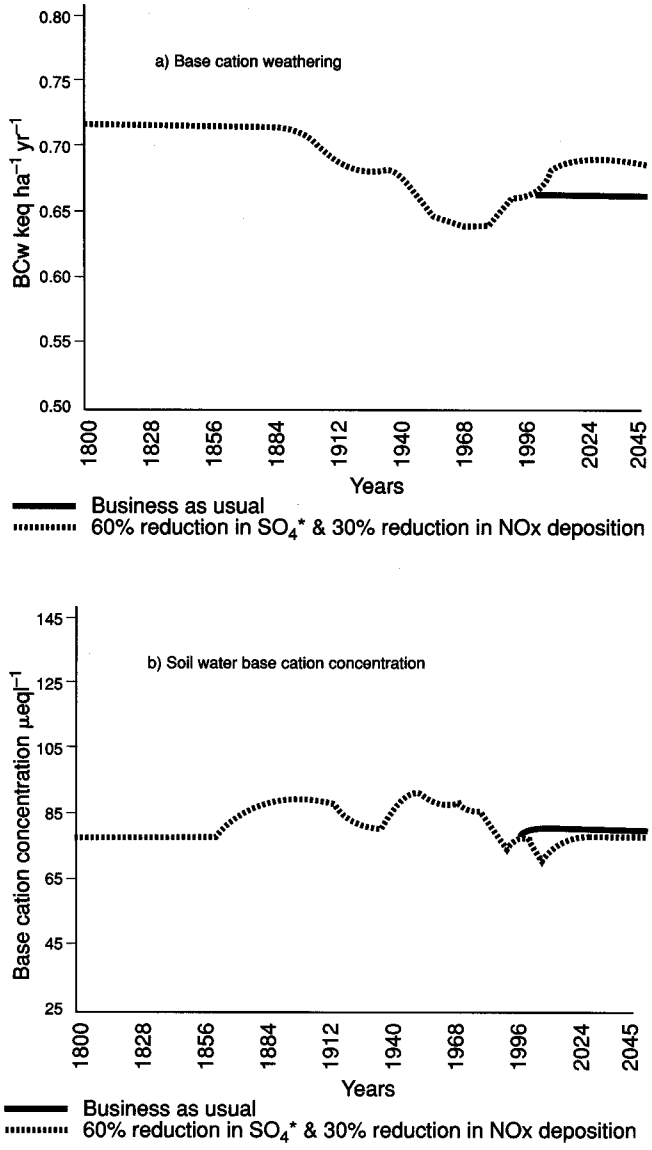

Fig. 4. *Predicted a) Bs horizon base cation weathering and b) soil water base cation concentration for an acid grassland stagnopodzol at Plynlimon.*

Table 5. (Ca+Mg+K):Al_{crit} ratios for acid upland vegetation species (data from Sverdrup and Warfvinge 1993b).

Species	(Ca+Mg+K):Al_{crit}	Reaction type	K value
Holcus lanatus	8.0	Unspecific	1.5
Agrostis capillaris	1.0	Unspecific	0.2
Calluna sp.	0.8	Unspecific	0.2
Deschampsia flexuosa	0.5	Unspecific	0.13
Erica sp.	0.65	nd	nd
Vaccinium myrtilus	0.4	nd	nd
Juncus squarrosus	0.3	Unspecific	0.08

nd = not determined

details of the model derivations and experimental data used to formulate the damage functions are contained in Sverdrup and Warfvinge (1993b). Base cation–aluminium exchange for most of the species listed in Table 5 is simulated using the Unspecific ion exchange model which denotes that the reaction is valence unspecific, i.e. the ion exchange matrix is indifferent to the valence of the adsorbing ions and the matrix behaves as a continuum of receptor sites. This implies that when Al^{3+} exchanges for BC^{2+}, the difference in charge is adjusted for by some as yet unknown process. The damage function using the Unspecific model is expressed as:

$$f(BC/Al) = (BC/Al) / ((BC/Al) + Kus) \quad (4)$$

where:

Kus = response coefficient for the Unspecific model

The effect on plant growth is calculated by Sverdrup and Warfvinge (1993b) as a percentage reduction (G) relative to 'normal' growth:

$$G = \Sigma\, x(uptake)_i \,.\, 100 \,.\, (BC/Al)_i / ((BC/Al)_i + Kus) \quad (5)$$

where:

$x(uptake)_i$ = the fraction of uptake in soil layer i
$(BC/Al)_i$ = molar base cation to aluminium ratio in soil layer i

Equation 5 was solved for each plant species using the values of K given in Table 5, the uptake distributions defined in SAFE and the predicted (BC/Al) ratios from the model runs. For the majority of species, the predicted relative growth reductions are small, reaching a maximum of between 4 and 5% below 'normal' growth. The largest growth reductions are shown by *Holcus lanatus* (Fig. 5b). Growth is slightly below 'normal' under pre-industrial conditions reflecting the plant's tendency to grow on less acid soils. Relative growth declines to about 77% of normal between 1960 and 1970 although good recovery is predicted (to c. 90% of 'normal') as acid inputs decline.

The relationships between acidification and growth used above are defined under controlled laboratory conditions,

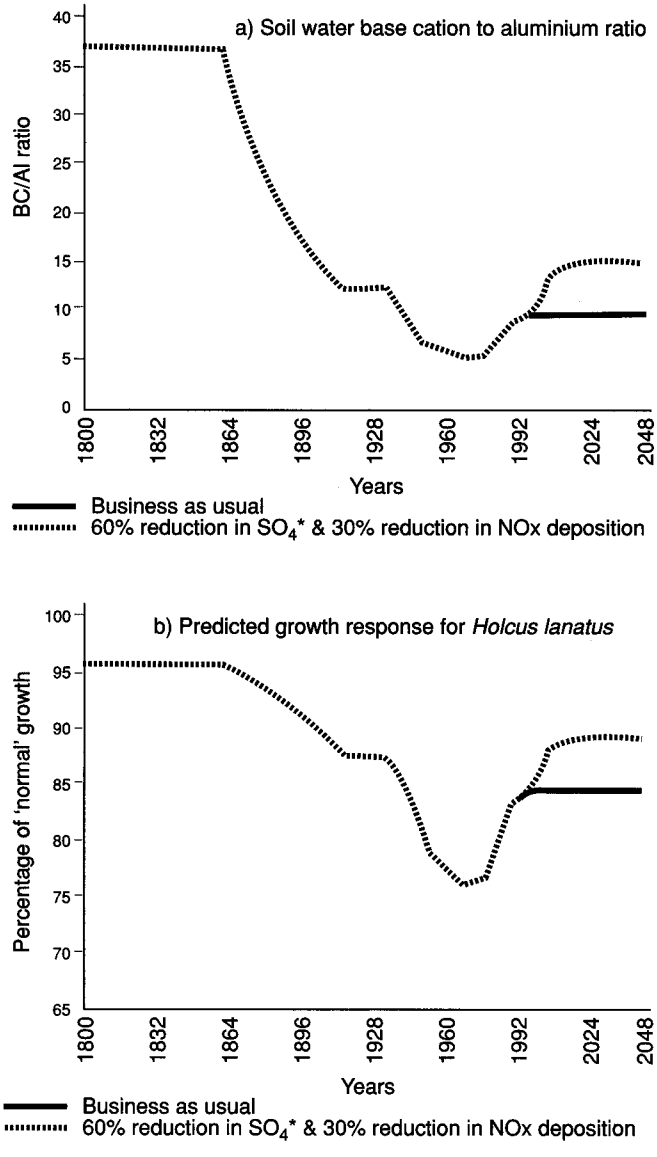

Fig. 5. *Predicted a) Oh horizon soil water base cation to aluminium ratio and b) growth response for* Holcus lanatus *growing in acid grassland at Plynlimon.*

and uncertainties always surround extrapolation of such data to the field situation. The model does not include the anticipated effects of secondary stress factors such as changes in tolerance to frost or drought, it does not include other chemical interactions, for example between aluminium and phosphorus nor does it allow for the effects of competition between plant species growing in a sward. Sverdrup and Warfvinge (1993b) also point out that there are considerable uncertainties surrounding some of the data used to define the growth relationships. It would seem best, therefore, to treat these predictions with caution, as indicative of the likely responses and for comparing responses between species of different 'acid' tolerance.

The (Ca + Mg + K):Al response function used here is not accepted universally and has been subject to recent criticism (Hogberg and Jensen 1994). In a more recent review, Cronan and Grigal (1995) concluded that the (Ca:Al) ratio could provide a useful ecological indicator of 'the approximate thresholds beyond which the risk of forest damage from aluminium stress and nutrient imbalances increases'. They recommend a more conservative approach using other complementary indicators (e.g. soil base saturation less than 15% of effective CEC) to corroborate observations of Ca:Al ratios. In view of its central role in critical loads methodology as the link between predicted soil chemistry and plant response, it is important that further work should be undertaken to evaluate the concept.

Uncertainties in Model Predictions

It is generally difficult to confirm the accuracy of the model predictions. However, there are some independent data and the SAFE predictions can be compared with those from the MAGIC model applied to the C2 catchment.

Soil chemical data were collected from the site in 1984–1985 and, in general, there is good agreement between the observed and modelled values (Table 6). These observations were made close to the calibration year, so perhaps this is not surprising. Compared to observed data, the model underpredicts base saturation in the Oh and C horizons. At that time (1984/1985), buffered, neutral, molar ammonium acetate was used to determine exchangeable base cations whilst exchangeable acidity was measured using unbuffered potassium chloride. The results of the two analyses were combined to yield the effective CEC of the soil. A subsequent comparison of results obtained using neutral ammonium acetate and unbuffered ammonium chloride suggested that the neutral ammonium acetate extraction probably overestimated the exchangeable base cation status of the soils due to the presence of pH dependent charge surfaces. This resulted in an overestimate of CEC and base saturation (Luo 1990). The underprediction in the C horizon is less readily explained. The large (50%) over-prediction of base cation concentrations in the Bs horizon may indicate that modelled weathering rates are too high or that insufficient uptake or leaching is occurring. Because of the complex interactions between the various model parameters, it is very difficult to isolate a single cause in this case.

The MAGIC model has been run at the C2 catchment (Whitehead *et al.* 1988) and predicts a weathering rate of 2.05 keq ha^{-1} $year^{-1}$, approximately twice the 250 year average value for the soil profile predicted by SAFE (0.94 keq ha^{-1} $year^{-1}$). Despite the differences in weathering rates, MAGIC predicts an initial base saturation for an aggregated single soil 'box' of 18% in 1840, declining to 4% in 1984; this compares well with the SAFE predictions.

The difference in weathering rate predictions reflects the contrasting approach between the two models and

Table 6. Comparison between observed and modelled soil chemical conditions for 1984–1985.

	Observed	Modelled	Observed	Modelled
	Oh horizon		Eag horizon	
pH	4.11	4.00	4.26	4.18
Base saturation (%)	37	14	4	8
ANC (μeql^{-1})	–60	–74	–80	–72
(Ca+Mg+K) (μeql^{-1})	61	54	68	54
Ca+Mg+K/Al	10.8	7.8	2.8	2.6
	Bs horizon		C horizon	
pH	4.36	4.51	4.70	4.87
Base saturation (%)	5	5	22	6
ANC (μeql^{-1})	–63	–46	–59	–45
(Ca+Mg+K) (μeql^{-1})	47	80	67	84
Ca+Mg+K/Al	2.4	3.2	1.9	2.3

provides complementary information about the functioning of the catchment. The MAGIC model provides a lumped representation of the C2 catchment in which weathering rates are variables tuned to fit observed present-day stream and soil water chemistry. In contrast, SAFE has been applied to a representative soil profile and weathering rates are calculated on the basis of soil mineralogy and biogeochemistry. The stream water chemistry of the C2 catchment is influenced by diffuse sources of base cations at the head of the stream (Chapman 1994); these may be related to groundwater inputs. MAGIC accommodates these by increasing the weathering rate, but these base cation sources are not represented in SAFE as they occur below the soil profile. The contrasting results have important implications for understanding of the acidification response of upland catchments. Low predicted weathering rates imply that the soil may recover only very slowly under reducing acidic inputs; stream water chemistry, however, is influenced by deeper (groundwater) sources of base cations which will continue to provide buffering against acidic inputs.

The weathering rate predicted by SAFE agrees well with the average weathering rate (1.52 keq ha^{-1} yr^{-1}) obtained from applications of the PROFILE model to stagnopodzol profiles developed on Lower Palaeozoic greywackes throughout the UK (Langan *et al.* 1996). Whilst this is not surprising given that PROFILE forms the weathering sub-model of SAFE, it gives a measure of confidence in the values and assumptions used to run SAFE at Plynlimon. The SAFE weathering rate is, however, approximately 2.4 times the value of 0.39 keq ha^{-1} $year^{-1}$ presented by Langan *et al.* (1996) as the average calculated using element depletion techniques. However, the latter are not without errors, especially in relation to the age and assumed long-term stability of the soil profile.

There are considerable uncertainties in a number of parameters within the SAFE model. Those identified in work relating to PROFILE apply equally to the geochemical weathering sub-model in SAFE. Sensitivity analyses of PROFILE model applications to Scandinavian sites (Jonsson *et al.* 1995) and at Plynlimon (Zak *et al.* 1997) indicate that variations in soil bulk density, volumetric water content and exposed mineral surface area have major consequences for predicted weathering rates. Soil mineralogy and climatic data have less effect. Thus, the assumptions concerning illite and the temperature data at Plynlimon are probably less important than the uncertainties surrounding the soil physical quantities. Of the latter, soil moisture is the least well known value at the Plynlimon site whilst exposed mineral surface area is extremely difficult to measure accurately. For SAFE, the other main areas of doubt are in the construction of the nutrient cycling component of the model and in the deposition time-series.

Despite long-standing ecological research in the UK, consistent published data for litter fall nutrient return, net mineralisation and canopy exchange for upland semi-natural acid grassland systems are not readily available. In particular, the response of these components to changes in deposition, as well as to other factors such as rainfall is not well known. Furthermore, the sensitivity of the model to variations in these parameters has not been fully investigated.

In these model runs, the pattern of excess calcium deposition follows that of excess sulphur, i.e. base cation supply is reduced alongside acidic inputs reflecting the uncertainty in the reconstructions of historic deposition trends, particularly for excess base cations and ammonium. This is an important topic to address nationally if dynamic acidification models are to be used in connection with critical loads and the assessment of recovery from acidification. In addition, future trends in excess base cations need to be resolved; for example to what extent should excess base cation deposition patterns be tied to those of excess sulphur?

An investigation of the effects of varying the pattern of excess calcium deposition over time has been undertaken using the simple hypothetical historical time-series for calcium deposition shown in Fig. 6. This time-series assumes a small excess calcium deposition of 2.7 meq m^{-2} yr^{-1} in pre-industrial times resulting in a total deposition of 15 meq m^{-2} yr^{-1}. From 1860, calcium deposition was increased linearly to 1987 amounts (30 meq m^{-2} yr^{-1}) and held constant at this amount into the future. The model was then re-calibrated using the modified calcium inputs but all other parameters were unchanged from the earlier runs. Future predictions under the 'business as usual' and reduced acid pollutant input scenarios were made keeping calcium deposition constant at 1987 levels.

The results of the model runs are summarised in Fig. 7 and 8. Modelled initial conditions in 1800 show a very small difference between the two calcium deposition scenarios. A slight improvement in predicted soil chemical conditions in 2050 is achieved by maintaining calcium deposition at 1987 levels under the reduced acid deposition scenario. The time-series of soil chemical conditions in the Bs horizon predict more acidic conditions between 1920 and 1940, with very little difference in conditions

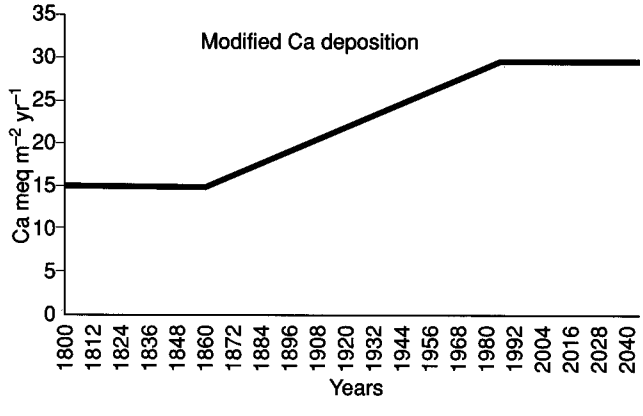

Fig. 6. *Simplified hypothetical deposition time series for calcium.*

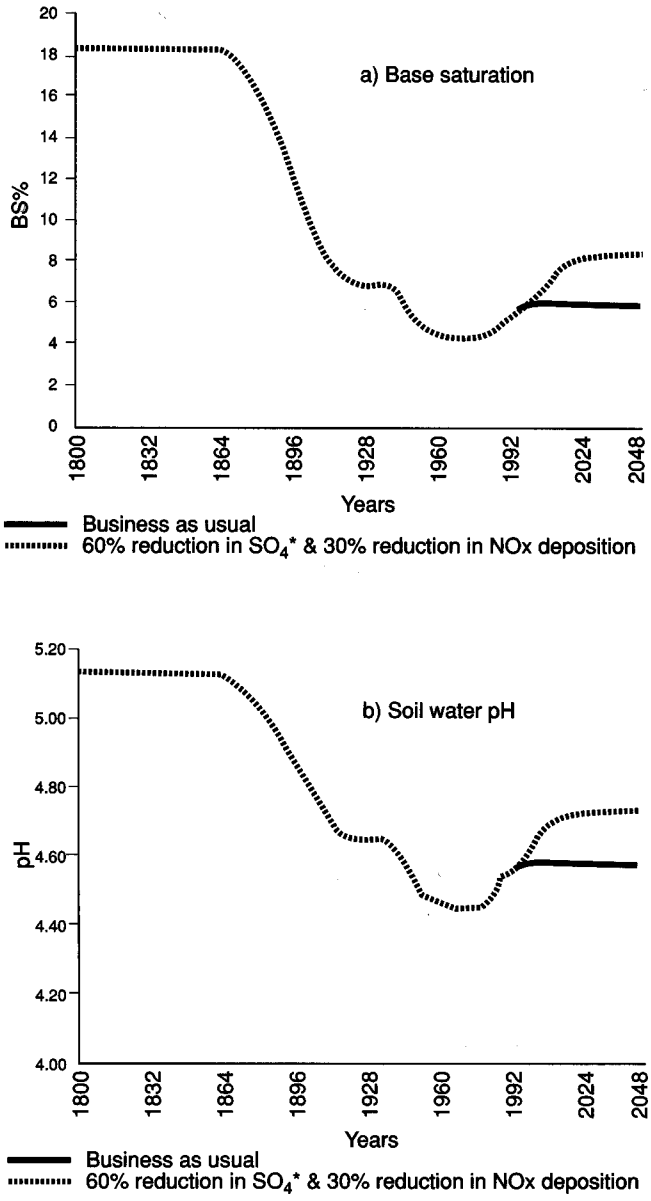

Fig. 8. *Predicted a) Bs horizon soil water ANC and b) soil water base cation to aluminium ratio for an acid grassland stagnopodzol at Plynlimon using calcium deposition time series shown in Figure 6.*

between 1960 and 1980 (cf Fig. 2 and 3 with Fig. 7 and 8). These differences reflect the lower calcium inputs which result from the slower, linear increase in deposition from 1860 to 1987 (Fig. 6) compared to the large inputs in Fig. 1a. The results suggest that the model as configured for these applications is relatively insensitive to changes in calcium deposition which amount to c. 20 meq m^{-2} yr^{-1} of Ca in the 1960s and 1970s.

Conclusions

The SAFE model has been calibrated and run at an acid grassland site at Plynlimon. The site is representative of large parts of the uplands of mid-Wales where landuse has remained substantially unchanged for many decades and therefore provides a reasonable indication of the likely progress of soil acidification due to acid deposition. The model predicts that soils became increasingly acidified with the onset of acid deposition in the mid 19th century although some recovery was predicted as deposition declined in the late 1970s and early 1980s. This recovery is accelerated as deposition is reduced further in line with proposed cuts in emissions. However, even with reductions in excess sulphate and NOx depositions to 40% and 70% of 1980 levels respectively, recovery in the subsoil is still slow with base saturation values at about 50% of pre-acidification values by the year 2050. This is consistent with the very low weathering rates estimated for the base-poor soil parent materials in the region.

The model predicts that acidification has had little effect on the growth of native acid grassland plant species. However, substantial growth reductions (upto 23%) are predicted for more acid sensitive species which might otherwise have grown satisfactorily under pre-industrial soil acidity conditions.

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